

# Pervaporative Separation of Volatile Organic Compounds from Water: Boundary Layer Resistance Modeling

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**Abstract:** The rapid industrialization over the decades has resulted in environmental pollution. Water resources are more and more contaminated by volatile organic compounds (VOCs) coming from the process industries. Conventional processes like air stripping and adsorption with activated carbon, extraction, biological treatment, distillation are found to be moderately successful in VOC/water separation, mainly when the concentration of the VOC is very low and when the quantity of effluent to be treated is large. Membrane separation processes are now considered as a better substitute to separate trace VOCs from dilute aqueous solutions. A detailed mathematical model based on resistance-in-series model was formulated to evaluate the influence of liquid boundary layer, membrane and vapor phase resistances on overall mass transport for pervaporative separation of VOCs from dilute aqueous solutions. The performance equation for the entire module was derived by simplifying the mass and momentum balance on both the feed and the permeate sides. The obtained set of non-linear ordinary differential equations coupled with the solution-diffusion model was solved numerically for the pervaporative separation of toluene and 1,1,1-trichloroethane from dilute aqueous solutions through shell and tube type hollow fiber module containing poly(dimethylsiloxane) (PDMS) membranes as tubes. From the results it was found that the liquid phase boundary layer plays a significant role in overall mass transport.

**Index Terms - VOCs, Pervaporation, hydrophobic membrane, resistance-in-series model, influence of boundary layer**

## I. INTRODUCTION

Water pollution is one of the major challenges that is being encountered globally. The wastewater coming from various chemical industries are contaminated by VOCs, particularly aromatic hydrocarbons (e.g. Benzene, Toluene, Phenol, ether etc.) and halogenated hydrocarbons (e.g. chloromethane, Chloroethane, chloroform, etc.). Removal of VOCs by conventional technologies is not economically viable. In the recent times, membrane separation processes grabbed more attention for the separation of organic components from wastewater. Pervaporation (PV) using a suitable hydrophobic membrane is a better alternative compared to other membrane separation processes for such applications [1]. PV is a membrane based process in which separation of liquid mixtures is achieved by contacting feed liquid mixture with the upstream side of a non-porous perm-selective membrane, solute dissolves and diffuses in the membrane, and the permeate which is enriched with the preferentially permeating component is removed as a vapor at the downstream side. Difference in the feed pressure and the vacuum applied on downstream side provides driving force for the separation of species [2]. In this process no intermediate or by-products are formed, so it is an environmentally attractive process. The other main advantages of using pervaporation for VOC-water separation is that it is technically feasible, and economically viable process. The pervaporation procedure framework for isolating VOCs from wastewater is shown in Figure 1.

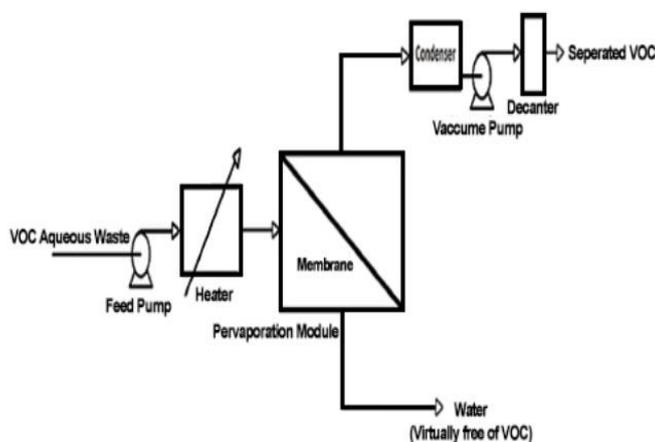


Fig.1: Pervaporation process for VOC removal from water

Elastomeric polymers that are hydrophobic in nature, mainly Polydimethylsiloxane (PDMS) or silicone rubber is most commonly used for these applications [3]. In industrial applications, membranes are generally made in the form of flat sheets, plate and frame, spiral wound and hollow fiber modules. Mostly shell-and-tube heat exchanger type hollow fibers are used for pervaporative separation of VOCs from dilute solutions. In hollow fiber membrane module bundle of fibers are enclosed in a shell. They promise more rapid mass transfer due to their high-packing density. They are self-supported, have self-contained vacuum channel and are economically superior in comparison with other modules [4], [5]. Based on the system requirements; the feed mixture is sent either on the shell side or on the bore/tube side of a hollow fiber wall and is removed down the fiber bore. In the present study, shell side flow configuration is considered, i.e., the feed fluid is applied to the outside (shell side) of the fibers, and the permeate passes through the fiber wall and is removed down the fiber bore as shown Figure 2.

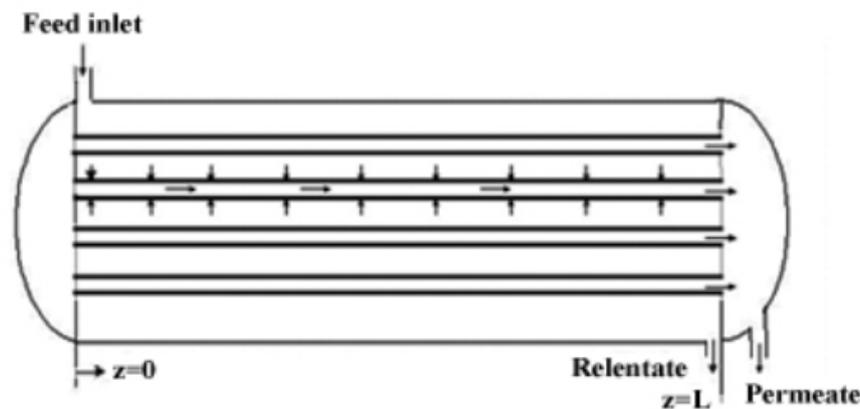


Fig.2: Hollow fiber module with shell side feed flow configuration

Pervaporation process can be influenced by several design and operating variables. Subsequently, for successful commercialization of a PV process these factors should be understood thoroughly. Identification of the controlling resistance in the overall mass transport is one of the critical factors in module design and process efficiency.

A.A. Ghoreyshi et al. [6] developed mathematical model for a flat sheet membrane based on resistance-in-series model. The results obtained show that the liquid phase boundary layer plays a significant role in overall mass transport for all cases under study and ignoring this contribution could lead to a significant error in design and scale-up applications.

B.Raghunath and S.T.Hwang [7] developed mathematical model for tubular membranes for the pervaporation of dilute volatile aromatic solutes from water. They inferred that when the membrane resistance to the transport of solute is low, then the liquid-phase boundary layer mass transfer resistance assumes significant importance by limiting the overall transport of the solute through the membrane.

J.G. Wijmans et al. [8], studied the role of boundary layers in the removal of volatile organic compounds from water by pervaporation through a spiral-wound membrane module. They have concluded that the boundary layer resistance is positive for components enriched in the permeate but is negative for components depleted in the permeate.

C.K. Yeoma et al. [9] carried out the permeation of chlorinated hydrocarbon/N<sub>2</sub> mixtures through PDMS membrane. From the analysis of the ratio of membrane resistance to boundary layer resistance, it was found that the boundary layer resistance becomes more important relative to the membrane resistance when feed flow rate is slower.

Psaume et.al [10] studied the extraction of trichloroethylene in dilute aqueous solutions by pervaporation was studied using silicone tubing as a membrane. It was observed that the concentration polarization at the liquid-membrane interface controls the mass transfer of the solute.

M. She, S.T Hwang [11], carried out experiments with flat sheet membranes to concentrate flavour compounds from dilute aqueous solutions. Modelling results showed that for the three dilute flavour compounds (ethyl butyrate, benzaldehyde, and trans-2-hexenal) studied, the boundary layer resistances were the same order of magnitude as the membrane resistances and therefore should not be neglected.

However, most of the earlier works were done for pervaporation through flat sheet membranes or tubular membranes. Hence, one of the objectives of this work is to formulate a detailed mathematical model of hollow fibre membrane module based on resistance-in-series model coupled with solution-diffusion mechanism for the pervaporation of trace organics from water. The second objective is to study the influence of each resistance on the overall mass transport of the system.

## 2. Theory

### 2.1 Flux Model

The resistance-in-series model combined with solution-diffusion model is used for estimating the permeate flux. According to solution-diffusion mechanism, the transport of all the species from bulk upstream side to bulk downstream side of a dense homogeneous membrane is described by five consecutive steps:

- 1) Diffusion of the components from bulk of the feed to feed-membrane interface.
- 2) Sorption of the component molecules into the membrane
- 3) Diffusion of the components through the membrane
- 4) Desorption of the components from the membrane into vapour phase on the permeate side.
- 5) Diffusion of the components from the membrane-permeate interface into the bulk of the vapour phase.

As shown in Figure 3, overall flux of species is a function of combined resistances of feed boundary layer, membrane, support and permeates side boundary layer.

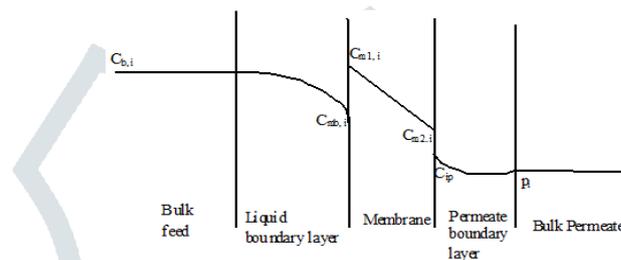


Fig. 3: Schematic representation of mass transport steps during pervaporation process

The support layer used for the process is considered to be highly porous; hence its contribution to the overall resistance is negligible. Low pressures are applied on the permeate side and the diffusion coefficient in the gas phase is greater than that in liquid phase by a factor of 104. Hence vapour phase resistance on permeate side is negligible. Thereby, the overall resistance to mass transfer is the sum of two resistances, namely, feed side boundary layer resistance and membrane resistance.

According to the resistance in series model, the overall mass transfer coefficient  $K_i$  at steady state is given by

$$\frac{1}{K_i A_m} = \frac{1}{k_{li} A_F} + \frac{t}{L p_{i,m} H_i A_m} \quad (1)$$

Where  $A_m$  and  $A_F$  are log mean membrane area and area of the feed boundary layer respectively.

$$A_F = 2\pi r_i L \quad (2)$$

$$A_m = 2\pi \bar{r}_L L \quad (3)$$

Log mean radius,  $r_L$  is given by

$$\bar{r}_L = \frac{r_0 - r_i}{\ln \frac{r_0}{r_i}} \quad (4)$$

Liquid phase mass transfer coefficient,  $k_{li}$  depends on hydrodynamic conditions and is estimated by Leveque correlations for laminar flow.

$$Sh = 1.62 \left( Re Sc \frac{d_{tube}}{L} \right)^{0.33} \quad (5)$$

For  $Re > 4000$ , it is obtained from the equation

$$Sh = 0.026 Re^{0.8} Sc^{0.33} \quad (6)$$

Where  $d_{tube}$  is the inner diameter of the fiber and  $L$  is the length of the fiber.

The overall mass transfer coefficient can be expressed as

$$K_i = \frac{L p_{i,m} H_i}{(E_i + 1)t} \quad (7)$$

The ratio of liquid boundary mass transfer resistance to the membrane resistance is defined by a dimensionless number  $E_i$ , and is given by

$$E_i = \frac{L p_{i,m} H_i}{k_{li} r_i \ln \frac{r_0}{r_i}} \quad (8)$$

The organic flux in terms of overall mass transfer coefficient is given by

$$N_i = K_i \left( C_{b,i} - \frac{p_i}{H_i} \right) \quad (9)$$

This can be rewritten as

$$N_i = \frac{L p_{i,m} H_i}{(E_i + 1)t} \left( C_{b,i} - \frac{p_i}{H_i} \right) \quad (10)$$

In similar way water flux is also analysed. Since water is abundant in the feed, concentration of water at the feed-membrane interface is almost equal to that of the bulk solution, i.e., there is no resistance for water in the liquid film. Expressing water flux in terms of partial pressure driving force

$$N_w = \frac{L p_{w,m}}{t} (P_w^{sat} - y_w p) \quad (11)$$

From Equation (3.27) it is evident that water flux depends only on downstream pressure for dilute aqueous solutions.

With dilute VOCs, the total flux is simply the sum of non-interacting component fluxes,

$$N = N_i + N_w \quad (12)$$

## 2.2 Mathematical model

The model equations are obtained by simplifying mass, species and momentum balance equations for shell side feed flow configurations. The obtained set of non-linear ordinary differential equations describes the variation of properties like pressure, velocity and composition along the fibre axial position. The transport equations are written both for the feed and the permeate side of the module since the flux depends on the conditions on both the sides. Vacuum is said to be applied on the downstream side at the end of the module. A cross-flow model was assumed in this study. The permeation through the membrane is said to take place in the radial direction.

The following assumptions are made to formulate the model equations:

- 1) Operation is isothermal
- 2) Deformation of the fibres under pressure (vacuum) is negligible
- 3) Steady incompressible flow of fluid is considered
- 4) Feed as well as permeate side variation in the radial direction is neglected, since the permeation flux in pervaporation is generally low
- 5) Negligible axial diffusion compared to convection

### Retentate side balances

The molar species balance on the feed side on simplification yields:

$$\frac{dx_{ib}^F}{dz} = \frac{2N(R_{tube} + t)}{v R_{shell}^2} V_{sl} \left( \frac{x_{ib}^F J}{M_{sl}} - \frac{J_i}{M_i} \right) \quad (13)$$

The overall mass balance on the feed side on simplification yields:

$$\frac{dv}{dz} = \frac{-2N(R_{tube} + t)}{R_{shell}^2} \left[ \frac{M_j J}{\rho_{jl} M_{sl}} + \left( \frac{M_i}{\rho_{il}} - \frac{M_j}{\rho_{jl}} \right) \frac{J_i}{M_i} \right] \quad (14)$$

The momentum balance on the feed side on simplification yields:

$$\frac{dp^F}{dz} = \frac{-2f \rho_{sl} v^2}{D_e} + \frac{2N(R_{tube} + t) M_i M_j v \left( \frac{1}{\rho_{il}} - \frac{1}{\rho_{jl}} \right) \left( \frac{x_{ib}^F J}{M_{sl}} - \frac{J_i}{M_i} \right)}{R_{shell}^2 \left( \frac{M_i x_{ib}^F}{\rho_{il}} + \frac{M_j x_{jb}^F}{\rho_{jl}} \right)} + \frac{4N(R_{tube} + t) \rho_{sl} v \left[ \frac{M_j J}{\rho_{jl}} + \left( \frac{M_i}{\rho_{il}} - \frac{M_j}{\rho_{jl}} \right) J_i \right]}{R_{shell}^2} \quad (15)$$

### Permeate side Balances

The molar species balance on the permeate side on simplification yields:

$$\frac{dy_{ib}^P}{dz} = \frac{2RT^P}{p R_{tube} u M_j} \left( \frac{J_i M_{sv}}{M_i} - J y_{ib}^P \right) \quad (16)$$

The overall mass balance on the permeate side on simplification yields:

$$\frac{du}{dz} = \frac{2RT^P \left( \frac{RT^P J_i M_{sv}}{M_i} - \frac{RT^P J_i M_j}{M_i} - RT^P J_{y_{ib}}^P - J u^2 M_j y_{ib}^P \right) - 2p M_{sv} u^3 f y_{ib}^P M_j}{p R_{tube} y_{ib}^P M_j (M_{sv} u^2 - RT^P)} \tag{17}$$

The momentum balance on the permeate side on simplification yields:

$$\frac{dp}{dz} = \frac{2RT^P u \left( M_{sv} J_{y_{ib}}^P - \frac{M_{sv}^2 J_i}{M_i} + M_j J_{y_{ib}}^P + \frac{M_{sv} J_i M_j}{M_i} \right) + 2p M_{sv} u^2 f y_{ib}^P M_j}{R_{tube} y_{ib}^P M_j (M_{sv} u^2 - RT^P)} \tag{18}$$

The friction factor is estimated by the following equation [12]:

$$f = \frac{16}{Re} \text{ where } Re = \frac{u D_{tube} \rho_{sv}}{\eta_{sv}} \tag{19}$$

**Boundary conditions:**

The properties of the retentate at the entrance of the module equal to the properties of the feed and hence the differential equations for the retentate (feed) side are subjected to the following boundary conditions:

$$P(0) = P_{in}; v(0) = v_{in}; x(0) = x_{in} \tag{20}$$

The differential equations for the permeate side are subjected to the following boundary conditions: permeate composition at the entrance equals the cross flow flux fraction since there is no bulk permeate stream at the entrance of the module; permeate velocity is zero at the entrance; pressure at the end of the module is equal to the applied permeate pressure.

$$y_{ib}^P(0) = \frac{J_i(0)}{J(0)}; u(0) = 0; p(L) = p_{ap} \tag{21}$$

where  $z = 0$  denotes the inlet point of feed and  $z = L$  is the outlet point of permeate collection respectively.

**3. Results and discussions**

The formulated model equations combined with the solution-diffusion model based flux equations were used to predict the performance of the hollow fibre module made of PDMS membranes for separating toluene and 1,1,1-trichloroethane from wastewater. The physical properties of the feed components are listed in Table 1. Operating conditions and fibre dimensions used in the present simulation are listed in Table 2.

Table 1 Physical property of feed components at 30°C

Property	Toluene	1,1,1-trichloroethane	water
Liquid density (kg/m <sup>3</sup> )	938.72	1447.10	995.38
Liquid viscosity (10 <sup>-3</sup> kg/m.s)	0.5248	0.5221	1
Vapor viscosity (10 <sup>-6</sup> kg/m.s)	7.098	9.462	9.406
Molecular weight (kg/mol)	0.092	0.1313	0.018
Henry's constant (kPa.m <sup>3</sup> /mol)	0.7358	2.1115	--
Permeability through PDMS membrane (10 <sup>-8</sup> mol.m/(m <sup>2</sup> .kPa.s) [13]	5.28	1.58	2.32
Diffusivity of solute in water (10 <sup>-9</sup> m <sup>2</sup> /s)	1.97	2.56	--
Heat capacity (J/mol.K)	157.44	145.09	34.25
Heat of vaporization (kJ/mol)	37.56	37.65	43.76

Table 2 Fiber dimensions and operating parameters used for the simulation

Parameter	x <sub>0</sub> , toluene	x <sub>0</sub> , TCE	Re	P <sub>app</sub> (Pa)	L (m)	R <sub>tube</sub> (µm)	t (µm)	N <sub>tube</sub>	T (°C)	P (Pa)
Value	9.8 x 10 <sup>-6</sup>	5.6 x 10 <sup>-6</sup>	20	200	1	450	50	2.5 x 10 <sup>5</sup>	30	20x10 <sup>5</sup>

The resultant set of non-linear differential equations coupled with flux equations is to be solved numerically for a given feed system to get the variation of properties like pressure, velocity and composition of the species along the fiber axial position. The chief inspection is that, it is a two point boundary value problem, i.e., feed side is an initial value problem while the permeate side

is a boundary value problem. Therefore, a trial-and-error shooting method is used to solve the problem. For a specified permeate pressure at the end of the module, the boundary value problem is converted to an initial value problem by guessing the unknown pressure on the permeate side at the entrance of the module. Euler integration of the corresponding permeate pressure equation is carried out to acquire its value at the end of the module, i.e., at  $z = L$ . The obtained value is then compared with the actual boundary condition, and the integration is repeated with a new guess pressure at  $z = 0$  until a convergence of tolerance  $1e-5$  is observed with respect to calculated and applied values of permeate pressure. The spatial co-ordinate  $z$  is discretized into 12000 parts. It is observed that further reduction of the step size of  $z$  has no effect on the simulation results. For every shooting value of downstream pressure at  $z = 0$ ; the flux equations of species are to be solved simultaneously to obtain downstream mole fractions. This is accomplished using multi-variable Newton-Raphson technique. The code simulations are carried out using MATLAB software.

Figure 4 shows a linear plot of variation of component flux along the fibre axial position. Then the variation of overall resistance with membrane thickness were plotted in Figure 5 to determine the individual liquid and membrane phase mass transfer coefficients.

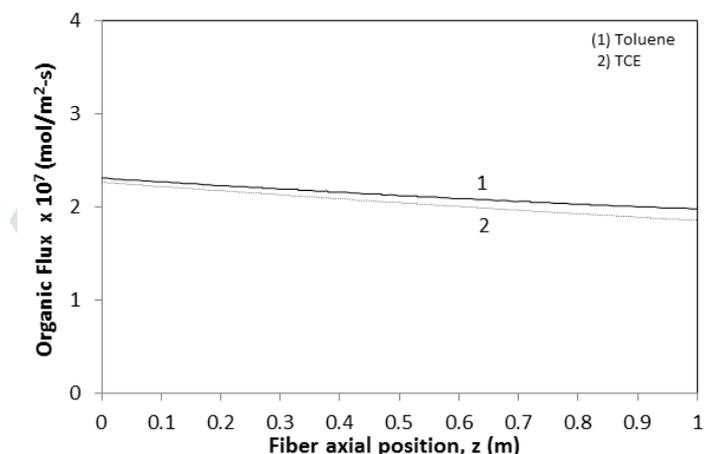


Fig. 4: Variation of organic flux along the fibre length (at the values mentioned in Table 2)

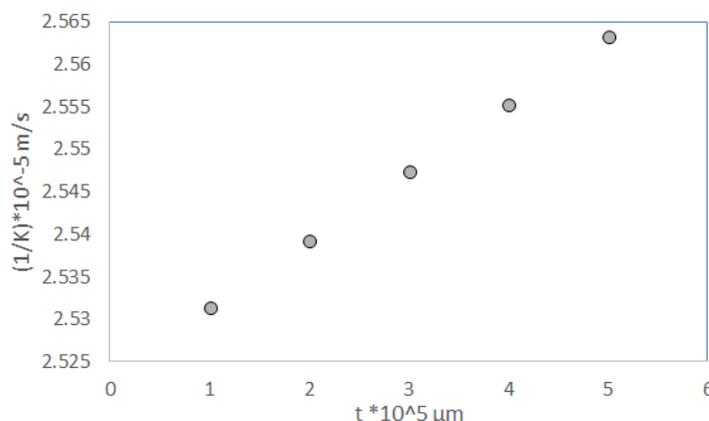


Fig. 5: Plot of the overall resistance vs. membrane thickness for toluene-water system

Parameters like liquid boundary layer mass transfer coefficient, overall mass transfer coefficient, and the ratio of liquid boundary layer resistance to membrane resistance are estimated and presented in Table 3. From Table 3 it can be inferred that liquid phase mass transfer resistance (reciprocal of mass transfer coefficient) is less than that of membrane resistance.

Table 3 Liquid boundary layer, membrane phase and overall mass transfer coefficient

Solute	$L_m$ [13] ( $10^{-8}$ mol.m/(m <sup>2</sup> .kPa.s))	$k_l$ (m/s)	$K_i$ (m/s)
Toluene	5.28	$3.802 \times 10^{-6}$	$3.901 \times 10^{-6}$
Trichloroethane	1.58	$4.531 \times 10^{-6}$	$4.641 \times 10^{-6}$

Alternatively, the role of boundary layer resistance can be quantified by calculating the contribution of liquid phase resistance to the overall resistance from Equation 8 and are given in Table 4. Values of  $E_i$ , liquid boundary layer resistance to membrane resistance are found to be  $>100$ . This indicates that mass transfer resistance of the liquid boundary is more than that of the membrane and hence significantly affect the overall resistance of the process.

Table 4 Fraction of liquid phase resistance from total resistance

Solute	$k_i/K$	$E_i$
Toluene	0.9746	198.2
Trichloroethane	0.9763	142.8

Feed side boundary layer is found to be the rate controlling step in the removal of VOCs from water and has great effect on the separation efficiency of pervaporation process.

## CONCLUSION

In this study, model equations are formulated for the pervaporative separation of trace organics from dilute aqueous streams through a hollow fibre pervaporation module based on resistance-in-series model. An expression was derived for overall driving force based on individual resistances that depend on hydrodynamic conditions. These values are easily accessible since the bulk fluid phase properties are known. An investigation is made to evaluate the importance of boundary layer resistance in the vapor permeation. It is concluded that the influence of liquid phase boundary layer on overall mass transport is high and must be taken into account in the design of a membrane module.

## Notations

A	area ( $m^2$ )
$d_{tube}$	inside diameter of the fiber(m)
$D_e$	equivalent diameter (m)
E	dimensionless number
f	friction factor
H	Henry's law constant ( $kpa.m^3/mole$ )
J	mass flux ( $kg/m^2s$ )
K	overall mass transfer coefficient (m/s)
k	mass transfer coefficient(m/s)
L	length of the fiber (m)
$L_p$	permeability ( $mol.m/m^2.kpa.s$ )
M	molecular weight (kg/kmol)
N	permeation molar flux ( $kmol/m^2.s$ )
P	pressure (pa)
$p^{sat}$	Saturation pressure (pa)
R	universal gas constant ( $J/mol.K$ )
$r_i$	inside radius of the tube (m)
$r_o$	outer radius of the tube (m)
$r_L$	log mean radius of the fiber
$R_{shell}$	radius of the shell (m)
$R_{tube}$	radius of the tube (m)
Re	Reynolds number

Sc	Schmidt number ( $\mu/\rho D$ )
Sh	Sherwood number ( $kL/D$ )
T	temperature (K)
t	membrane thickness(m)
u	permeate velocity(m/s)
v	feed velocity(m/s)
V	molar volume ( $m^3/mol$ )
x	retentate concentration(mole fraction)
y	permeate concentration(mole fraction)
z	axial coordinate of the fiber

**Greek letters**

$\delta_{bl}$	boundary layer thickness
$\eta$	viscosity (kg.ms)
$\rho$	density(kg/m <sup>3</sup> )

**Subscripts**

0	initial
L	end of the module
ap	applied
b	Bulk liquid feed
bl	boundary layer
F	feed side
i, j	organic species
in	inlet condition
l	liquid phase
m	membrane
sl	liquid mixture
sv	vapor phase mixture
tol	toluene
TCE	trichloroethane
tube	tube or fiber
w	water

**Superscripts**

F	feed side
P	permeate side



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